Abstract No. quar205

EXAFS Studies of Nonheme Iron Enzymes, Reaction Intermediates, and Model Compounds

L. Quaroni, J.-U. Rohde, K. Koehntop, and L. Que, Jr. (U. of Minnesota)

Beamline(s): X9B

Model Compounds and Reaction Intermediates: High-valent iron-oxo intermediates are frequently invoked as the key oxidants in the oxygen activation mechanisms of iron enzymes that carry out the two-electron oxidations of alkanes to alcohols and of olefins to epoxides. In the catalytic cycle of soluble methane monooxygenase (MMO) the key intermediate is a diiron(IV) species called **Q**. In the course of our biomimetic efforts, we have generated the first synthetic diiron(IV) complex with an Fe_2O_2 diamond core, providing the synthetic precedent for such a core in MMO-**Q**. EXAFS analysis of this compound, which decomposes above –80°C, reveals an Fe···Fe distance of 2.8 Å, comparable to values found for other high-valent complexes with $M_2(\mu\text{-O})_2$ cores. A short Fe–O scatterer at 1.8 Å indicates an oxo bridge. Taken together with other spectroscopic data the complex is formulated as $[Fe^{IV}{}_2(\mu\text{-O})_2(L)_2]^{4+}$ [1]. We also have obtained EXAFS data on its metastable Fe^{III} alkylperoxo precursor.

Nonheme Iron Enzymes: The EXAFS spectra of some binary and ternary complexes of ferrous ACC oxidase with ascorbic acid, ACC and bicarbonate have been recorded. These experiments comprise part of a larger set aimed at describing the interaction of the iron center with substrates and cofactors. The complex of the protein with ascorbic acid shows that this substrate binds in the proximity of the metal center and affects its coordination geometry. It is not clear whether direct binding to the metal occurs or whether the geometrical changes are due to an indirect perturbation of the first coordination sphere. Also spectra of the ternary complexes with ascorbic acid/ACC and with bicarbonate/ACC have been recorded. Analysis of the data is still in progress.

Acknowledgements: This work was supported by grants from NIH and NSF.

Reference: [1] Miquel Costas, Jan-Uwe Rohde, Audria Stubna, Raymond Y. N. Ho, Luca Quaroni, Eckard Münck, Lawrence Que, Jr., "A Synthetic Model for the Putative $Fe^{IV}{}_2O_2$ Diamond Core of Methane Monooxygenase Intermediate Q," *manuscript submitted to J. Am. Chem. Soc.*